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The temperature scanning reactor
III: Experimental procedures and data processing

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Abstract

The theory of Temperature Scanning Reactors (TSRs), presented in full elsewhere [1–3], is free of virtually all approximations which would limit its utility in kinetic studies. This is not to say that temperature scanning (TS) is free of difficulties when the theory is implemented in practice. Below we discuss the features of an experimental TS reactor in operation in our laboratories and present experimental procedures and data-handling techniques which deal with the real-life difficulties encountered in using temperature scanning. The operation of real temperature scanning reactors is confronted by the practical realities of dealing with hardware limitations, uncertainties in calibration, signal noise and other such difficulties which, in this type of operation, pose very different problems from those encountered in conventional kinetic experiments. In particular, there is much new ground to be broken in learning how best to deal with TS kinetic data, which are more akin to a signal, in the sense used in data transmission for purposes of communication, than to the individual experimental data points we are accustomed to collecting in conventional isothermal kinetics research. We report here on some of our efforts to deal with these problems, for example, through the use of signal filtering, two dimensional splining and other mathematical techniques, some of which are new to the field of kinetics. The temperature scanning method itself is very new, so that it comes as no surprise that the data interpretation and visualisation methods which it entails, and its operational requirements, will pose unfamiliar challenges to both experimentalists and theoreticians for some time to come.

Keywords: Data filtering; Temprature scanning; Kinetics; Experimental methods

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1. Introduction

In previous papers [3,4] we have described the theory and operation of various temperature scanning reactors: Batch Reactors (TS-BR), Stream-Swept Reactors (TS-SSR), Continuous Stirred Tank Reactors (TS-CSTR) and Plug-Flow Reactors (TS-PFR). Computer simulations of the operation of these reactors have been presented elsewhere [3] to provide numerical examples and to illustrate the very different and unfamiliar appearance of the data one collects from these "kinetics instruments". Of course, computer simulations provide ideal, perfect data: no set-point uncertainties in reactor control; no noise in the measurement of the parameters being monitored; and no calibration errors.

In real experiments these are all difficulties to be dealt with. This paper describes some of the experimental procedures and data-handling

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considerations which apply to the various temperature scanning reactors. In many cases, particularly in the reactor types which produce rate data from a single reactor run (i.e., TS-BR, TS-SSR and TS-CSTR), the temperature scanning procedure can be very forgiving of controller inaccuracies and noisy measurements. For the TS-PFR, which requires assembling data from several reactor runs before rates can be extracted, considerably more care is needed in order to smooth its noisy data, but even in this case some controller inaccuracy need not be a serious problem. What must be made free of noise in all cases are the signals being monitored for purposes of determining the rate of the reaction; most particularly, the signals communicating the composition of the product mixture.

In the following sections we first consider the ''single run'' reactor types, showing that precise control of temperature or flow rates is not a very important issue, and that in these cases even the fluctuations produced by noisy analytical instruments are easily dealt with. We then consider the rather more difficult case of the TS-PFR. We describe in some detail the experimental TS-PFR used in our laboratory, including the reactor configuration, the control procedures and the measurement of output composition. Finally, we describe which aspects of the operation do not need to be controlled with any great precision, and which must be regulated precisely.

To quantify the issues raised, we consider the smoothing of noisy data. The simple ''smoothing'' or ''filtering'' of the curves of collected data that is satisfactory for ''one run'' reactor types must be replaced in TS-PFR operation by a more sophisticated filtering that takes account of the fact that rates are calculated from an assemblage of data over several different reactor runs.

We round out our discussion by presenting an analogy of TS-PFR operations to cartographic surveying of landforms. This perspective will be familiar to anyone who has had the opportunity to read contour maps, and may be useful in understanding the difference between TS operation and conventional isothermal kinetics experiments. It should make it clear why we choose to think of a TSR as a ''Kinetics Instrument'', not just an ''experimental reactor''.

2. Single-run reactors: TS-BR, TS-SSR, TS-CSTR

2.1. Process control considerations

For the TS-BR, once the reactor has been loaded and the reaction begun, the only control imposed is that on the temperature. The operator may wish to use this temperature to drive the reaction into various desired regions in the Conversion–Temperature plane (sometimes called the ''reaction phase plane'') but, whatever the temperature, it has no affect on the calculations used to extract rates. These calculations require only a measurement of the conversion, the internal temperature and clock time: a (X,t,T) triplet, discussed previously when the theory of TSR operation was described [3,4]. Thus, the accuracy of the temperature controller is irrelevant to the rate calculations, although of course it may affect how successfully the reaction can be driven to the desired regions.

For the TS-SSR, as for the TS-BR, the external temperature or the temperature of the sweeping fluid may be used to help drive the reaction into desired regions, but once again this has no effect on the rate calculations. It is the temperature of the reacting solid that matters. Consequently precise temperature control is not required. In practice it may be difficult to measure the real reaction temperature of the solid sample. This is a problem well known to makers and operators of TPD equipment and other similar apparats where solids are the reactant. We will not comment here on the sophisticated methods that have been developed elsewhere to deal with this problem.

Similarly the velocity of the sweeping fluid in the TS-SSR need not be controlled precisely, so long as it is fast enough to prevent any significant back-reaction. Depending on how the conversion data are being collected, it may not even be necessary to measure or record this sweep-fluid velocity. This will be the case if $N(t)$, the amount of reactant remaining in the reactor at time t, or $P(t)$, the rate at which reaction product is exiting the reactor at time t, can be measured directly. However, if $P(t)$ is calculated, say from composition measurements of the exiting fluid, then it becomes necessary to measure and record the sweep-fluid velocities, although it is still not necessary to control them precisely.

For the TS-CSTR, the operator may freely vary the inlet fluid temperature, the external temperature and the inlet flow rate. The goal of controlling these is once again to drive the reaction into various desired regions of the X–T plane, but precise control is not required as long as the correct flows and temperatures are recorded. In fact it is not necessary to record the external temperatures at all; only the correct inlet and the internal (or outlet) temperature need to be recorded at all times, and in liquid-phase reactions it is not even necessary to record the inlet temperature. In gas-phase reactions this measurement is necessary to allow a calculation of the gas–volume expansion due to changes in temperature.

2.2. Data smoothing considerations

All three "single-run" reactor types require continuous (or, practically speaking, almost continuous) monitoring and recording of the temperature of the reaction (and possibly the inlet temperature), the clock time (or input flow rate) and the extent of conversion (plus product composition if we are interested in selectivity). We now consider these in turn.

2.2.1. Temperature

As can be seen from the rate calculation formulas in papers presenting the theory of temperature scanning [2,3], temperature measurements enter only marginally into the calculation of reaction rates in "single run" reactor operation. For example, they enter as a correction to the concentration term due to volume expansion caused by temperature changes. High precision in temperature measurement is therefore unnecessary. We need only identify the temperature at which the reaction is taking place, a measurement which is often acceptable at an accuracy of $\pm 2°C$. Standard thermocouples linked through standard data boards can give sufficiently accurate measurements for this purpose. Of course, the more accurate and precise the measurement, the better the data-set.

2.2.2. Flow rate

Flow rates are most significant in rate calculations for the TS-CSTR, since space velocity is a key factor in the rate equation for that reactor. However, since changes in space velocity are normally made relatively slowly, continuous monitoring of flow rates easily allows for small fluctuations or random measuring inaccuracies to be filtered out by, for example, simple "moving-window" averaging.

2.2.3. Conversion

Measurement of conversion is potentially the most delicate measurement in the TS-BR and TS-CSTR since, for both of these reactor types, calculation of the rate involves calculation of the derivative of conversion with respect to time. Numerical differentiation of digital signals is notoriously sensitive to noise in the data. Even the presence of "digital dither", a scatter due to the resolution of the digital signal by the available electronics, can cause grief. Various instrumental techniques may be employed to measure conversion, but each is subject to random error and often there is unacceptable digital dither induced by the electronic components.

For instance, in experiments reported elsewhere involving the hydrolysis of acetic anhydride [5], conversion was calculated from conductivity measurements using available computer interface boards. Some noise in the con-

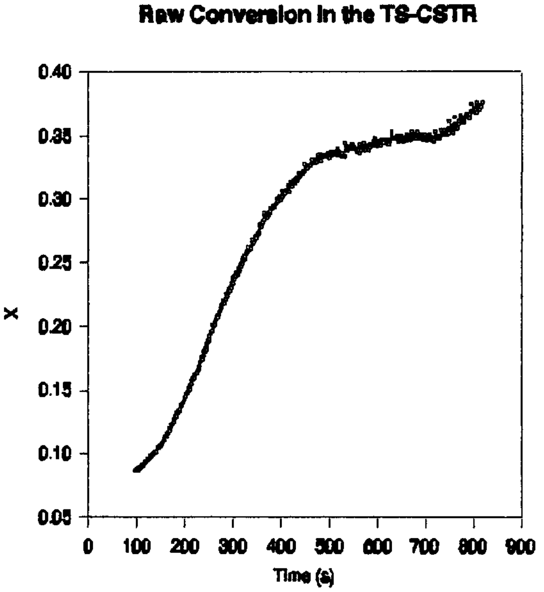


Fig. 1. The raw data of conversion (X) versus clock time (t) for the hydrolysis of acetic anhydride in a TS-CSTR.

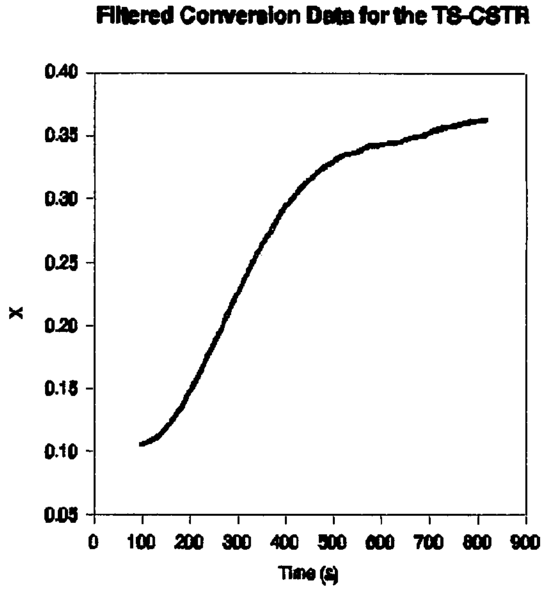


Fig. 2. The smoothed data of conversion (X) versus clock time (t) for acetic anhydride in a TS-CSTR.

ductivity signal was unavoidably present due to the electrodes used. In addition, digital dither was generated by the poor (12 bit) resolution of the data acquisition board. Fig. 1 shows the resulting, somewhat noisy, plot of conversion versus time. Clearly a naive numerical point-by-point differentiating to estimate $\mathrm{d}X/\mathrm{d}t$ would greatly amplify the noise. Various more sophisticated procedures to estimate $\mathrm{d}X/\mathrm{d}t$ must be contemplated, ranging from a simple moving-average filtering of the raw data followed by numerical differentiating, to least-squares-polynomial spline-fitting followed by analytic differentiation of the fitted polynomials. What turned out to be quite satisfactory in this case was a moving average over a window of about 5 points (about 1% of the total data collected). This procedure was repeated a number of times until the data were judged to be sufficiently smooth. Fig. 2 shows the smoothed X–t curve, while Fig. 3 shows the resulting $\mathrm{d}X/\mathrm{d}\tau$ versus t curve. Care must be exercised in this procedure to make sure that the filtering operation does not distort the underlying shape of the curve.

Confirmation that the underlying curve has not been distorted can no doubt be obtained objectively using appropriate statistical measures. On the other hand, we have found that a satisfactory judgement can be obtained from a

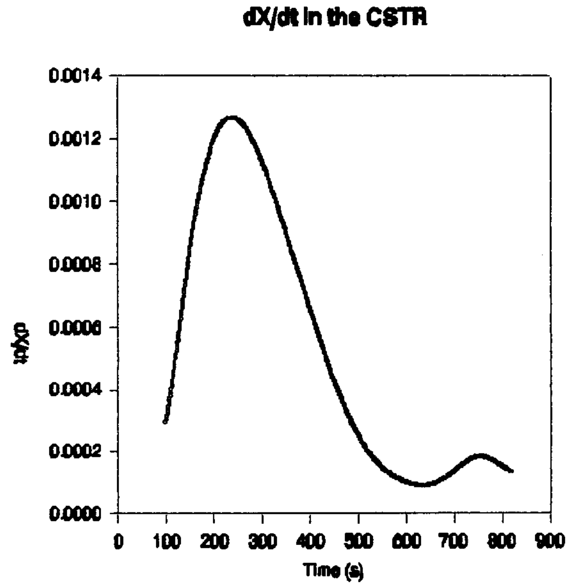


Fig. 3. Reaction rate (r) versus clock time (t) in the TS-CSTR.

visual inspection of the superposition of the smoothed curve over the raw data. We find this procedure to be quite adequate for practical purposes; however, it requires operator judgement in what otherwise promises to be a fully automated operation. If fully automated operation is found to be preferable, one can resort to appropriate statistical measures.

In other reaction systems there may be no such (relatively) ''quiet'' way of measuring conversion. In the experimental TS-PFR in our laboratory, a mass spectrometer is used to measure the mass spectrum of the total output stream in order to determine output composition. This information is used to quantify the composition of the output stream, using calibrations for individual components of the stream and solving a matrix equation to ''deconvolute'' the mole fraction of each individual component in the stream. The mass spectrometer itself produces rather noisy data and the deconvolution procedures can add to that noise. Even then, for a TS-CSTR the composition signal can be satisfactorily smoothed by a low-pass ''moving-window'' type of filter.

For the TS-SSR, there are several ways that $\mathrm{d}X/\mathrm{d}t$ might be measured. Some arrangements can give $\mathrm{d}X/\mathrm{d}t$ directly, and some give X from which $\mathrm{d}X/\mathrm{d}t$ is obtained by numerical differentiation. In either case, simple moving-window filtering works perfectly well. This type of configuration should be least sensitive to noise from any source.

2.3. Data filtering

All TSRs produce data in an almost continuous stream, making the traditional duplicate runs and estimates of variances (commonly used to estimate the size of the error in one-point-at-a-time kinetic experimentation) impractical and perhaps even inapplicable. The data stream from a TSR resembles a signal rather than data points — with noise superimposed on the message that the signal carries. The goal is therefore to remove the noise without distorting the message. This is done by filtering, a technique well established in communication technology but new, as far as we are aware, to chemical kinetics research.

Filtering is not the same as fitting a polynomial to scattered (noisy) data, a procedure frequently used in obtaining empirical descriptions of phenomena. Fitting to a polynomial imposes a shape on the underlying curve represented by the data. Since the TSR is a kinetics instrument, meant to facilitate fundamental research in chemical kinetics and mechanisms, we must not prejudge or arbitrarily impose the shape of the underlying curve. Filtering, as contrasted to fitting, is a procedure that averages the signal locally so that the true underlying trends and magnitudes of the signal are not altered.

If the filtering is done using a moving window averaging procedure, it is easy to see how it works. As long as the window is small in relation to the total data set, we remove the noise locally, without either forcing the overall curve to follow some preconceived polynomial or moving the average local point far from its experimentally determined position. If the window is too large — say it encompasses the whole data set — a moving window filter will also distort the true values, in this case giving the same value at each point.

Clearly there are many different filtering algorithms, some more appropriate to a given TSR than others. This variability in the optimal filter type and in the setting of its parameters arises because the nature of the noise depends on the hardware used in the given TSR, while the optimum filtering procedure depends on the nature of the noise. In time, the best filter for each TSR, and perhaps each reaction, will become better defined, using objective criteria, and will be implemented in appropriate circumstances.

For now, the standard filters which are available in the literature must be carefully examined for applicability to any given case and their efficacy judged largely by eye. As we have said, some day these issues will be better defined and justified with mathematical rigour so that the filters we presently use may well change. What will not change, and may become even more important, is the possibility of building cheap-but-noisy TSRs and compensating for this weakness in the hardware with highly effective filtering procedures. The filtering procedures can be easily implemented, at no additional cost, on the data-logging computer which is associated with each TSR. The trade-off between hardware and software is well known to communications engineers and bodes to be a feature of the TSRs of the future.

3. Operation of a multi-run reactor: the TS-PFR

A much more sophisticated and interesting situation arises with regard to data treatment when we come to use temperature scanning technology in TS-PFR operation. The PFR is the preferred reactor configuration in isothermal kinetic studies and is likely to persist in this role in temperature scanning operations. We illustrate the problem of data handling and reactor control in the TS-PFR by describing one of the many TS-PFR configurations possible: namely the gas-phase catalytic reactor configuration we have been using in our laboratories.

3.1. TS-PFR experimental apparatus

Our TS-PFR reactor system was supplied by SE Reactors Inc. and is shown in Fig. 4. On the left is the ''reactor module'' containing the reactor oven and control hardware; flow controllers, solenoids, back-pressure valve, data acquisition system, etc. On the right is the ''analytical module'', consisting of the mass spectrometer and hardware that make it a real-time gas analysis system. Each module is controlled by its own desktop PC computer.

3.2. The reactor module

The reactor module is instrumented with a number of thermocouples, mass flow meters and a pressure sensor. The flow meters and oven heaters receive control signals from the control computer which uses SE Reactors' TS software package operating under Windows®. In order to gather the signals required for the evaluation of reaction rates, we log various data

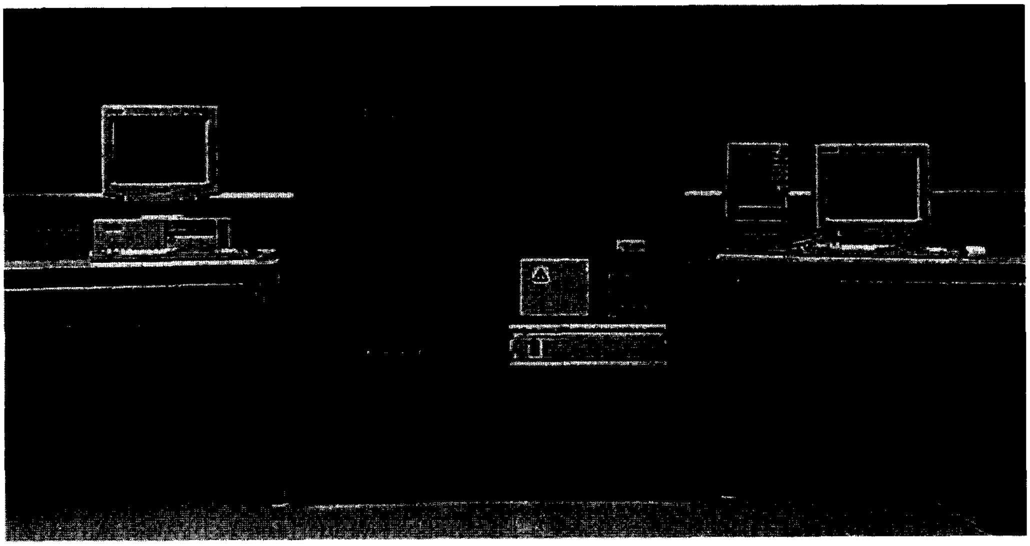
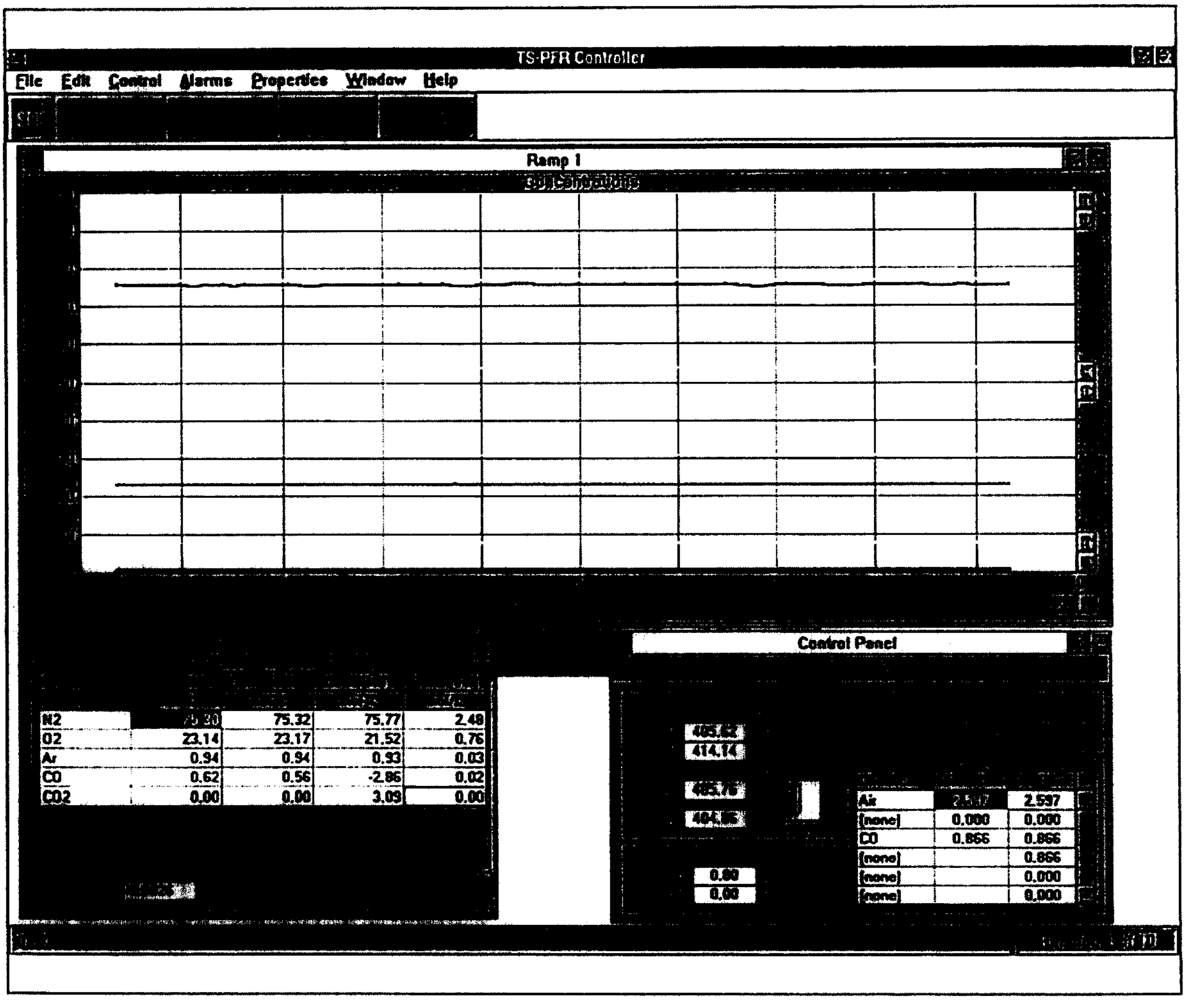


Fig. 4. A photo of the TS-PFR laboratory equipment.

streams on the control computer using the same integrated software package. The software receives the streams of signals from the various sensors via a commercial data acquisition system. This system is responsible for converting the analog signals from the sensors (thermocouples, mass flow meters) into digital form. The system we use includes both an analog-to-digital (A/D) converter and a D/A converter. Both capabilities are used, depending on the direction of information flow: i.e., whether signals are being logged from the equipment, or control commands are being sent from the computer.

The data acquisition system we use in our laboratories runs on a proprietary unit sold under the name I/O Plexer®. Each physical measurement and computer command signal is assigned to a specialized module on the I/O Plexer unit. For example, each temperature reading is assigned to a thermocouple module designed for that thermopair; each gas flow rate to a 0–5 V analog module; and so on. The I/O Plexer has its own on-board central processing



N2	75.30	75.32	75.77	2.48
O2	23.14	23.17	21.52	0.76
Ar	0.94	0.94	0.93	0.03
CO	0.62	0.56	-2.86	0.02
CO2	0.00	0.00	3.09	0.00

Air	2.597	2.597
[none]	0.000	0.000
CO	0.866	0.866
[none]		0.866
[none]		0.000
[none]		0.000

Fig. 5. The operator's control and display screen from the gas-phase catalytic TS-PFR.

unit which allows it to convert and assign all of the I/O signals from the 16 modules it operates, to appropriate elements.

The next link in the data-flow connects the I/O Plexer to the computer. This completes the connection from the physical world of reactor operations to the digital world of the computer. We do this using a null-modem serial cable between the I/O Plexer and the RS-232 port on the computer. All digital signals between the control computer and the I/O Plexer are transmitted through this port. The collection and processing of the digital signals within the computer is controlled by our integrated software package. A screen-capture of one of the many displays from this control and data processing software is shown in Fig. 5.

3.2.1. *Temperature control*

Recall from the theory defining temperature-scanning that, in a TS-PFR experiment, all temperature rampings from run to run must be along the same trajectory. As a result, the oven temperature and the inlet feed temperature must be accurately controlled. With this in mind, a custom designed air-circulation oven is used; its design is similar to that used for chromatographic ovens. A fan circulates the air within the oven through a draft tube and over the reactor itself. Due to the low heat capacity of the air, oven temperature response is essentially immediate and follows our linear ramping program very well. In order to transfer the oven heat efficiently to the feed gases entering the reactor, a long, thin, low-thermal-mass preheater is used. Once the gases have passed through the reactor and the catalyst, a thermocouple positioned immediately under the catalyst bed measures the reactor outlet temperature and conveys this value through the I/O Plexer to the TS software.

3.2.2. *Flow and pressure control*

Reactor feed rate is controlled by three mass flow controllers. A set-point is sent from the control software, via the I/O Plexer, to each of the flow controllers. The gas flows from the three flow controllers are mixed and sent through the pre-heater to the reactor. The total flow set-point is calculated by the control software to satisfy the operator's input of the required space times. This is sent to the individual controllers, after being apportioned to each controller according to the feed composition requested by the operator.

Pressure within the system is controlled by means of a back pressure control valve. The position of the valve needle in the back-pressure control solenoid valve is controlled by the PID controller built into our software, so the reactor pressure is maintained as smoothly as possible within the limits of hardware capabilities, aided by the tuning of the PID controller.

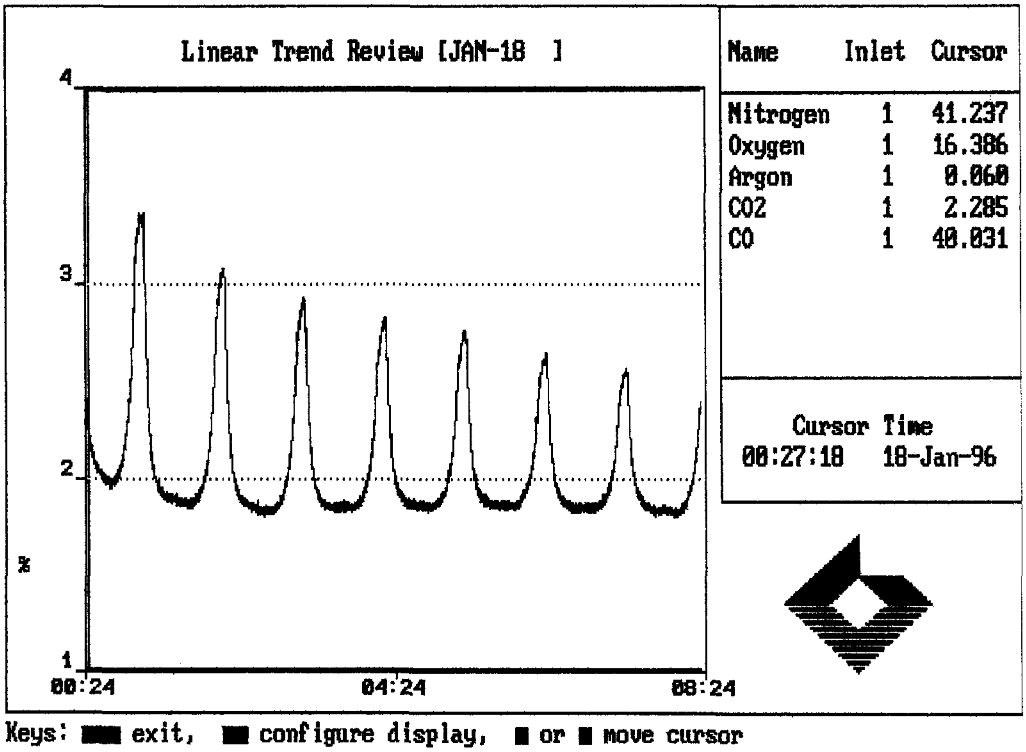
3.3. *Analysis module*

A physical link must also be made between the reactor and the mass spectrometer in the analysis module in order to collect samples of the reactor output for analysis of conversion, as required by the TS-algorithms. This is accomplished by introducing a capillary tube between reactor outlet and the mass spectrometer leak. One end of the capillary is placed directly below the centre of the catalyst bed immediately beside the outlet thermocouple. This ensures that no mixing of products or secondary reactions have occurred after the products exit the catalyst, and that the temperature at which products are collected is accurately recorded.

The analysis module consists of a 200 AMU quadrupole mass spectrometer supplied by FISONS®. Operation of the spectrometer is controlled by SensorLab electronics, whose instructions are input through the second computer attached to our TS-PFR. The physical signals coming from ions bombarding the electron multiplier detector in the MS are handled much the same way as the I/O Plexer signals. A voltage is generated by the ions hitting the detector. This voltage is put through an analog-to-digital converter dedicated to the MS, which produces a digital signal that is transmitted to and recorded by the MS control computer.

Using this method of analysis, very frequent (in the order of 1 every 6 seconds) analyses of the gas mixture leaving the reactor bed are possible. This yields the "almost continuous" conversion signal mentioned earlier. The sampling rate for purposes of TS-PFR operation must be frequent enough that no kinetic information is lost between analyses. In most cases, one analysis per degree of temperature ramp will suffice, so that our temperature ramping rates normally do not exceed 10 degrees per minute. A run ramping up over a 200°C range therefore takes 20 minutes; with cool-down, 30 minutes are required per ramp. An experiment consisting of 10 ramps takes 5 hours of automated operation. In cases where the analysis methods are slow, ramping rates must be reduced, increasing the duration of each TS experiment. Even if an experiment were to take 100 times as long (i.e., 600 seconds per analysis), the massive data base made available by this procedure would still make TS methods worth applying. Under such circumstances, the average TSR-derived rate data-base could be obtained within about 20 days of round-the-clock automated operation.

The raw data collected by the mass spectrometer consists of intensities at each mass number that is scanned. These intensities can be used to calculate the composition of the mixed gases exiting the reactor, using calibration spectra for the pure components which must be taken before the experiment is performed. This procedure involves a computational "deconvolution" of the spectrum of the mixture. Once the deconvolution is done, the resulting gas composition is available for further processing. A screen capture of the mass spectrometer control soft-



Name	Inlet	Cursor
Nitrogen	1	41.237
Oxygen	1	16.386
Argon	1	0.060
CO2	1	2.285
CO	1	40.031

Cursor Time
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Fig. 6. The mass spectrometer screen showing the output CO_2 concentration from one gas-phase catalytic TS-PFR experiment involving the catalytic oxidation of CO.

ware is shown in Fig. 6. There one can see one of the components of the exit stream being recorded in strip-chart format in real time.

3.4. TS-PFR control considerations

Stable and accurate control of flow rates are required in the TS-PFR, since one needs to perform several runs at various fixed flow rates whose ratios must be well known. However, the precise values of the flow rates do not need to conform very accurately to the intended values; miscalibrations in the flow settings do not much matter, as long as we know the ratios between flow rates. It is also essential to hold the flow rate constant throughout each run.

This applies to the usual TS-PFR setup in which each run is performed at some constant space velocity. In the more elaborate variable-flow-rate type of TS-PFR experiment described elsewhere [3], one needs to ensure that the space velocities in the various runs are carefully regimented according to the requirements of theory. In that case, more accurate flow control is essential. Fortunately, well-calibrated mass flow meters can do this with a minimum of difficulty.

As for temperature control of the inlet feed and external temperature, the actual temperature ramp profile used during a run does not matter; it can be linear or nonlinear, up or down, or both. However, the ramp does need to be reproduced exactly for each run in a TS-PFR experiment. This too is not a problem; heaters and temperature sensors combined with a PID controller can reproduce temperature ramps with satisfactory precision. Computer controlled heaters in appropriately designed ovens can easily generate linear ramps, and with a bit more programming of the control software can generate controlled nonlinear ramps as well. In the operation of our reactor, ramping rates of 10°C/min are achievable up to +450°C.

3.5. TS-PFR data smoothing considerations

As indicated previously, conversion in the TS-PFR is calculated from composition measurements made with a mass spectrometer. This results in fairly noisy X–t curves for each of the runs (see Fig. 7). It is tempting to smooth each of these curves separately, for example by some moving average scheme, and then to numerically calculate the derivatives needed to get the

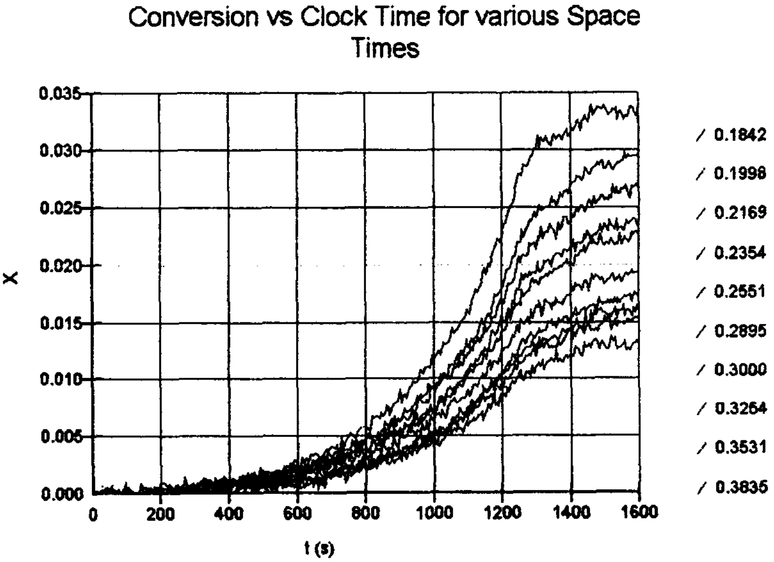

Fig. 7. The raw data of conversion (X) versus clock time (t).

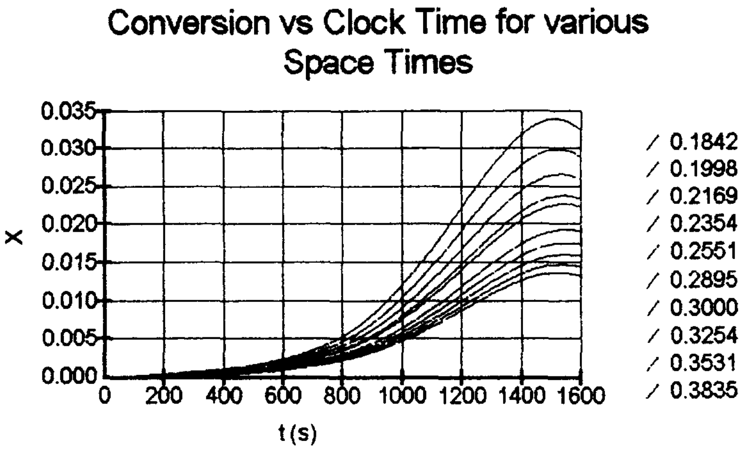

Fig. 8. One-dimensional smooting of individual curves of conversion (X) versus clock time (t).

rates. Fig. 8 shows such filtered curves, and they do look very smooth. Unfortunately this does not give satisfactory rate results. The difficulty is that the necessary derivatives are not along each X–t curve, but rather across the various curves so that $\mathrm{d}X/\mathrm{d}\tau$ values can be obtained.

To see this, consider Fig. 9, which is a smoothed 3-dimensional (3D) version of Fig. 7. This figure represents a smoothed version of conversion data one gathers from a TS-PFR in the following way. In any given run of a TS-PFR experiment, the TS-PFR is operated with feed flowing at a given fixed rate. As the run progresses, the temperature of the feed is ramped with clock-time (t) in some fashion. The outlet of the plug-flow reactor corresponds to some space time τ. For each (t,τ) combination there is a corresponding conversion (X). This means that one collects (X,τ,t) triplets at the outlet of the reactor operating at space time τ. By repeating this procedure at various values of feed rate, one obtains a series of such curves at various values of τ. This repetitive procedure scans the

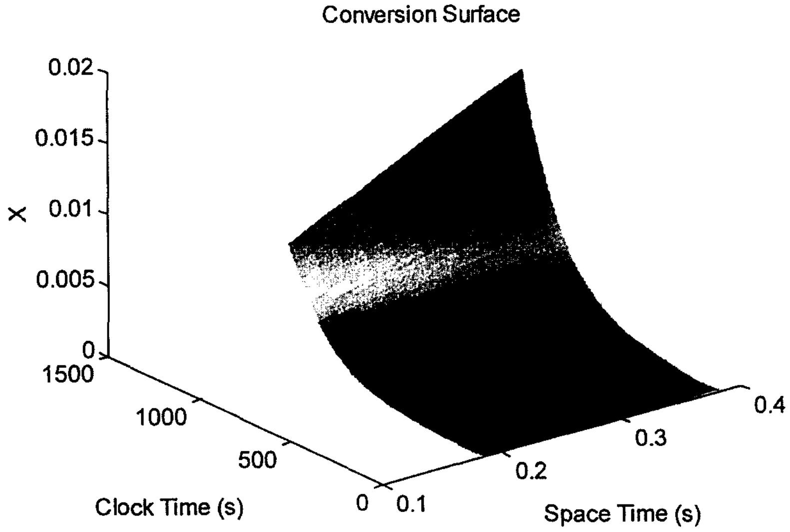

Fig. 9. A 3-dimensional representation of the smoothed conversion (X) data from Fig. 8 (clock time 0 to 1200 s only).

surface in Fig. 9 and defines it as well as one may require, depending on data logging rates and the number of scans.

A slice through the surface on Fig. 9 for any fixed clock time t_i gives the conversion conditions along a "virtual reactor" whose operation at the time t_i is at a constant input temperature T_{in} (which always occurs at that time, since the ramping is identical for each run), and at various conversions X each corresponding to a different space time.

At the same time t_i in each of the runs, there occur various output temperatures T_{out} which result from the influences of the thermochemistry of the reaction and the heat transfer between the reactor and its surroundings. In this way we may assemble triplets of $(X,\tau,T_{\mathrm{out}})$, data suitable for plotting on a subsequent 3D plot in these coordinates.

Returning attention to the (X,τ,t) surface, the slope of this surface along a constant t_i slice gives $\mathrm{d}X/\mathrm{d}\tau$, which is the reaction rate, at the output temperature T_{out} and the conversion X at the point in question. Therefore, we can immediately obtain (X,r,T) triplets which can be plotted in these new 3D coordinates.

These procedures are at the root of the numerical difficulties of the TS-PFR: it is not the slopes $\mathrm{d}X/\mathrm{d}t$ at constant τ that are required. This would be easy to calculate, since the raw data are gathered continuously in clock-time t for various fixed values of τ. Any noise along these curves can be readily filtered by a moving window averaging procedure, as is recommended for the "single run" reactors. Here, however, one requires the slopes $\mathrm{d}X/\mathrm{d}\tau$ at constant t. These are much trickier to evaluate, since along any of these fixed-t curves the data are more sparse. The number of data points available in this direction is just the number of scans in one TS-PFR experiment; typically about ten.

If the X–t curves in Fig. 7 were each smooth and accurate, then one could confidently compute the desired $\mathrm{d}X/\mathrm{d}\tau$ values by, say, fitting a spline to the (sparse) X–τ data for any fixed t, and computing the derivative analytically from the fitted spline. Indeed, this is the procedure used with good results in the computer simulations. Clearly this simple method cannot be used on noisy data such as that shown in Fig. 7. It is tempting to simply smooth the data along each of the X–t curves and then apply the cubic spline fitting, but as mentioned above this turns out to be unsatisfactory in practice; the rates so calculated tend to have troublesome fluctuations that are an artifact of the filtering procedure exaggerated by the spline fitting. Smoothing each curve independently ignores the fact that all the curves in fact lie on some smooth surface (Fig. 9); this procedure would lose enough information that subsequent splining of the sparse data in the X–τ direction would result in unreliable rates.

Rather than the one-run-at-a-time filtering, it is best to apply 2-dimensional filtering to the whole surface at once. Fortunately the data are available on a rectangular (t,τ) grid, so it is easy to apply available bicubic spline filtering techniques [6]. Algorithms for efficient filtering of surfaces, and for differentiation of filtered surfaces, are available as FORTRAN subroutines on the Internet [1].

In practice, these filtering routines require that the operator specify a "smoothness" parameter S that controls the trade-off between filtering to obtain a very smooth surface and filtering so that the smoothed surface follows the noisy data very closely, albeit not as smoothly. In general, it is impossible to auto-

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[1] For example, a subroutine called REGRID is available from NetLib. The Internet address for NetLib is http://www.netlib.org/. The FORTRAN subroutines are named REGRID, BISPEV and PARDER. REGRID is used to evaluate the nodes of the smoothing spline as well as the interpolating spline coefficients. BISPEV is a BIvariate SPline EValuation routine, used to evaluate the smoothed surface values, using the spline coefficients determined by REGRID. PARDER is a PARtial DERivative calculation, where a partial derivative in one dimension may be performed. Application of these subroutines is detailed in each of the FORTRAN files which can be downloaded in ASCII format.

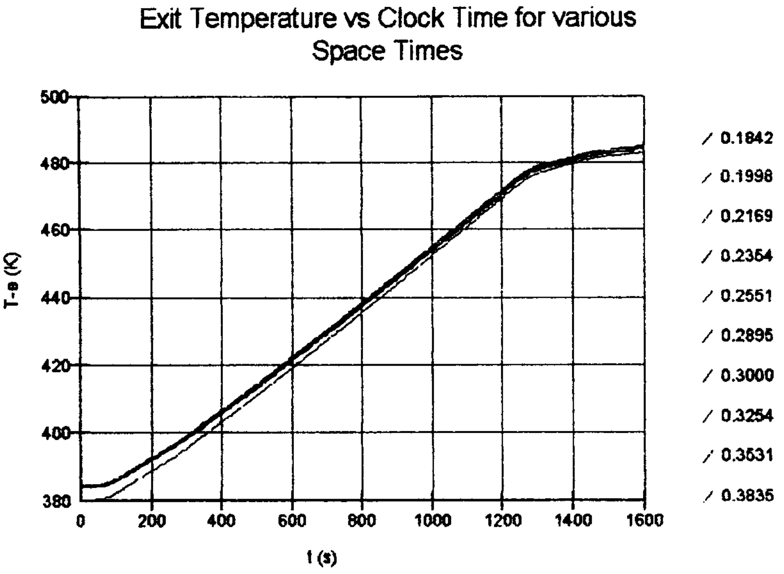

Fig. 10. The reactor exit temperature (T) versus clock time (t).

mate the optimal choice of S. The best advice is to view the generated surfaces graphically for various values of S, and make a visual determination of which surface is ''just smooth enough''. In fact, since we need to take slopes $\mathrm{d}X/\mathrm{d}\tau$, our experience suggests that it is better to use a slightly-more-than-just-smooth-enough surface. Fig. 9 shows the result of fitting a smoothing bicubic spline to the data of Fig. 7.

The optimal choice of the smoothness parameter S depends directly on the variance of the noise in the (X,τ,t) triplets. This variance depends in a complicated way on the variance of the noise in the raw output data, which is mostly generated by noise in the mass spectrometer amplified in a non-linear way in the calculation required to arrive at the product composition. Nevertheless, it seems likely that this noise is relatively constant from one experiment to another, and that an experienced operator will be able to make rapid estimates of the optimal value of S. Fortunately the goodness of fit of the rates is not very sensitive to small changes in S, so a reasonable estimate of the optimal S is sufficient.

Similarly, the measured exit temperatures during each run will have some noise, but much less than conversion measurements, and the noise is far less consequential since temperature does not enter in any sensitive way in the rate calculations. Fig. 10 shows a typical set of temperature-time curves for various runs.

In order to proceed with the data processing, it is necessary to interpolate temperature values for selected (t,τ) combinations that are intermediate to measured points. Consequently it is convenient to fit a surface to the raw T–t–τ data using techniques such as those described

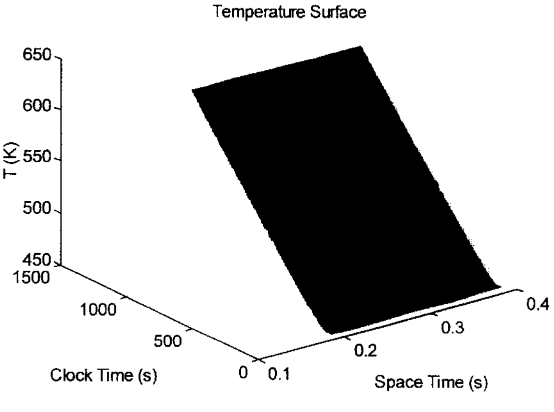

Fig. 11. A 3-dimensional representation of the reactor exit temperature (T) data from Fig. 10 (clock time 0 to 1200 s only).

above. Fig. 11 shows the result of applying a bicubic spline to the data of Fig. 10. In the end, the goal is a 3D surface in (X,r,T) whose constant r contours produce the better known ''reaction phase plane'' representation of constant rates on an X versus T plane.

3.6. *Acquisition and verification of results*

The results obtained from a TSR can be checked for the presence of extraneous influences such as diffusion or catalyst decay by repeating the experiment at different temperature ramping rates. In principle a pure kinetic rate will not be affected by the ramping rate and in such cases successive experiments at various ramping rates will yield exactly the same behaviour on the X versus T plane. The same procedure will yield a measure of the uncertainties in the experiment, although those should be insignificant in a well designed and operated TSR.

The TSR methods are valid with this level of confidence at all experimentally accessible conditions. The only limitations are those connected with the capabilities of the hardware. For example, the ramping rate will be limited by the power of the heaters, the design of the oven, and the heat transfer capabilities of the preheater.

A more constraining issue is the need to monitor the reactor output composition on a ''continuous'' basis. In this context continuous means at a rate which produces output compositions frequently enough so that the intervening temperature change is kinetically negligible. In most reactions one analysis per degree of temperature change is sufficient. In cases where the activation energy is very high or when multiple steady-states can occur, much more rapid analyses may be necessary. The need for rapid analysis for the TSR will provide an added incentive to develop the requisite analytical methods. At this time mass and infrared spectroscopes as well as a variety of electrodes, gravimetric and calorimetric methods are available to make a great many systems immediately amenable to TS studies.

4. Surveying by satellite: an analogy to TSR operations

The procedures used in TSR data treatment and the implications of the technological advances offered to kinetics by TS technology can be made more familiar by comparing them to the advances resulting from the introduction of satellite surveying in terrestrial mapping. The analogy is apt in that the behaviour of a reaction system on a given catalyst and at a fixed composition is confined to a surface resembling a hill or a ridge in three dimensions: conversion versus space time versus temperature. The equation which generates this surface is the integral of the kinetic rate expression. Surveying measurements used in the mapping of geographical terrain in the coordinates elevation versus latitude versus longitude are therefore analogous to the measurements made in a kinetics laboratory to determine the X–τ–T values, which are then used to determine the kinetic rate expression.

Conventional isothermal experimental methods in kinetics can be compared to early 19th century surveying methods. In those days surveyors travelled to the terrain on foot, or by mule or horse, or by boat, packing supplies, baggage, and bulky instrumentation, with the constant possibility of being beset by unexpected dangers and delays. At the cost of much hardship and adventure, the early surveyors measured enough points in the assigned terrain to draw a map which was adequate to guide a wagon train or even plan a railroad. One must admire their heroic efforts, but need not repeat them today.

Today, a surveyor can sit in an office and gain access to a satellite fitted with a sensitive altimeter which collects data points along traverses which lie under the satellite orbit. Combining these bands of data, and with the aid of signal filtering and appropriate data processing, extremely detailed 3D contour maps can be drawn of any terrain, including accurate information about slopes on the mountainsides: i.e., how steep is the grade in any direction within the area surveyed.

What satellite technology does for mapping, TSR ''instruments'' and software do for kinetic studies. Conventional reactor operations involve isothermal operation at steady state, at a series of space velocities, much like the point-at-a-time measurements of the 19th century surveyor. The resulting isothermal data set of $(X,\tau,T_{\text{const.}})$ is normally plotted as a graph of X versus τ at constant T. Let us for the moment imagine perfect and plentiful data so this plot is smooth and well defined. If one repeats this procedure at other temperatures (usually, no more than three are studied), one has a set of graphs of $X-\tau$ at various values of constant T. These sets of two-dimensional $X-\tau$ data can be combined in three dimensions where they will represent traverses at constant T of a three-dimensional surface with the coordinates X, τ, T. If one does a large number of densely documented traverses at various constant temperatures, the X–τ–T surface will be well defined (well mapped).

Unfortunately the conventional method of surveying a kinetic surface does not produce smooth and densely documented X, τ traverses; it produces only a few points along each traverse, not unlike the periodic position readings taken by old-time surveyors following predetermined survey lines over rough terrain. Surveyors in both situations will to try minimize time and effort by making the fewest possible traverses and readings to produce a usable result.

In kinetics, because each traverse is not smooth, conventional investigations treat each isothermal data set (or X, τ traverse) separately, by attempting to find a function which best fits the observed $X-\tau$ points of the traverse. In fundamental studies this function is meant to describe the kinetics of a proposed mechanism of reaction. If this ''rate expression'' is readily integrated, the raw experimental (X,τ,T) data can be fitted with the integrated form of the proposed rate expression directly. If the rate expression is not, or cannot be, integrated, one must first convert the experimental data triplets (X,τ,T) to the rate-containing triplets (X,r,T) where r is the rate of reaction at a fixed value of X and T.

The procedure for obtaining the rates in conventional experiments involves taking the derivative $\mathrm{d}X/\mathrm{d}\tau$ on a constant T curve, with sparse data points and experimental error superimposed. Since the available procedures for doing this are generally unsatisfactory, the most common simplification is to determine the rate near zero conversion (i.e., the initial rate of reaction); a few duplicate points at low conversion will yield a reasonable estimate of this quantity. In surveying terminology this is equivalent to determining the shape of the whole mountain by measuring the slopes of the foothills — not a satisfactory procedure in mapping mountains, and only somewhat more satisfactory in kinetic studies.

We now see that a rate of reaction is the slope on the ''X–τ–T_{outlet} mountain'', taken in the direction of a constant-T_{inlet} traverse of the surface; not an easy line to identify on this mountain, if the reactor is not isothermal, but nonetheless a traverse that is possible to identify in the operation of any reactor. In practice we find the correct traverses in a TS-PFR by looking for sets of points on the surface which correspond to the same ''clock time'' t_i. In this way we can collect as many traverses in the constant-T_{inlet} direction as we have t_i values in our raw data. Along each traverse we can calculate as many slopes as we wish. Hence the ''arbitrarily large number of rates'' that the TS-PFR makes available in a single experiment.

If we were able to determine by experimental methods the smooth shape of this mountain, we would be able to measure the slope at any point on its surface without further ado. The ''arbitrarily large'' number of (X,r,T_{outlet}) triplets would be immediately available for fitting to a proposed rate expression. The problem is that all survey results reflect the roughness of the terrain or, in kinetics, experimental error. To proceed, we must take the survey data and smooth it without distorting the underlying shape of the mountain. Too much smoothing, and we will have the map of a plane, leaving no trace of the original mountain.

In conventional studies, once the rate expression has been determined at one temperature, the same rate expression is fitted to the data at the other temperatures. If the fit is satisfactory, we proceed to the next stage of the mapping process. This involves determining the relationship between the rate parameters (kinetic rate constants and equilibrium constants) and the temperatures at which the various isothermal traverses were taken.

In theory, the relationship between individual traverses of an X–τ–T mountain must conform to certain forms of behaviour defined by the Arrhenius expression, but in practice the kinetic constants of the rate expression may appear in the rate expression as sums or more complex functions. Such kinetic parameters will not follow any predefined behaviour with temperature. The usual procedure therefore involves finding an empirical relationship between temperature and the rate constants. More revealing examination of the rate constants is made impossible by the uncertainties in the experimental data, and by its sparsity. This denies us some part of the information we seek if we mean to study reaction mechanisms.

Given this primitive state of the surveyor's art in kinetics, it is no surprise that kinetic terrain is ill-mapped, and that our knowledge of much of reaction kinetics resembles primitive maps rather than the detailed contour maps we now take for granted from cartographers. We can increase the available amount of data by sending out more surveyors, or by making them take more readings, but this is costly, time consuming, and remains subject to misadventure as well as human and instrumental error at each reading. How can we introduce modern surveying methods to the examination of kinetics surfaces? This is the issue the TSR technology is intended to address.

Due to the requirements of theory and hardware capabilities in the field of reaction studies, TS traverses as carried out by a TS-PFR do not lie along the traditional isothermal lines but along the constant T_{inlet} direction. This introduces a distortion into the X–τ–T surface which is similar to the distortion of physical terrain one would observe if the satellite traverses are recorded from an angle to the terrain rather than from directly overhead. The TS-PFR raw data must therefore be treated in a special way, as defined by theory, in order to extract the correct rates from this "distorted" raw data. The theory also tells us that steady state is not important in TS-PFR operations; as a result, our kinetics instrument can rapidly scan the kinetic terrain without having to hover over individual points before a reading is taken. With the large number of data points along each TS traverse made available by TSR techniques, signal filtering can be applied to smooth the profile of each traverse or of the whole terrain surveyed. One can easily take as many traverses as necessary to compile a very detailed and accurate picture of the reaction terrain, invoking no approximations or extrapolations.

Two-dimensional filtering procedures are available which filter the scanned surface in the two dimensions τ and T and yield calculated $(\delta X/\delta\tau)_{T\text{in}}$ slopes on the X surface. These are the slopes which correspond to rates of the reaction. A TS-PFR automatically provides not only the initial rates, but all rates which fall within the set of operating conditions studied, including rates at the high conversions — rates which are critical to industrial reactor design and operation. TS methods will also immediately reveal the effects of secondary reactions, inhibition by products, and other phenomena which are important in investigations of reaction mechanisms.

The single-run TSRs are even more flexible than the TS-PFR for data collection. These reactors can survey along almost any traverse and yield rates of reaction (slopes) along each individual traverse. It still takes a number of traverses to map the terrain in enough detail to draw a contour map (the X–T "reaction phase plane"), but now we can elect to follow only the traverses of greatest interest, rather than surveying a fixed grid of points, as we must do using a TS-PFR. The mapping analogy here is that the surveyor can chose to focus on a site of special interest and map this region in great detail, rather than surveying the whole territory.

With the masses of data made available by a TSR, rate expressions can be fitted with more confidence. It should also be possible to distinguish subtle differences between competing rate expressions, and hence between competing reaction mechanisms. Detailed knowledge of this sort will sharpen our insights into reaction mechanisms, and will surely bring many other as-yet unforseen benefits, perhaps opening up entirely new fields of study.

Using a TSR, a researcher is therefore in much the same situation as a modern cartographer, who sits in an office reviewing satellite data which is collected remotely and automatically, and then processes and interprets the masses of available data effortlessly using a computer program. The logged data can then be used to generate a map with enough precision, for example, to document and quantify continental drift. By dint of its ease of use and its unprecedented accuracy, satellite technology has opened up new fields of study and introduced a great deal of detail to the quantification of geography, geology, geochemistry, biology, and other fields. Although the equipment is much more complex than a theodolite, it can be used to map various features or of all regions of the globe simply by reprogramming the satellite's activities. Similarly, it takes but a few strokes of the keyboard or a new catalyst, or feed composition, to explore new reaction terrain using the TSR.

In the end, would anyone want to take the trouble of undertaking to do cartography the old-fashioned way? There seems to be a consensus in favour of satellite surveys in the cartographic and remote sensing communities. Those who will have tried both the TSR and isothermal methods of kinetic experimentation will have a chance to come to their own conclusions as to how well the cartographic analogy carries over to kinetic studies.

5. Conclusions

Temperature scanning technology provides a rapid and cost-effective method of obtaining unprecedentedly complete kinetic information about a broad range of catalytic and non-catalytic chemical reactions. In addition, the TS technology is remarkably robust in the face of controller uncertainties and measurement noise. The TS-BR, TS-CSTR and TS-SSR require only simple filtering of the conversion data to yield satisfactory rates of reaction. Flows too need to be controlled with no more than a modicum of precision

Only in the case of the TS-PFR does one have to be more than minimally careful about process control, or apply any but the simplest data-filtering techniques. For the TS-PFR, it is necessary to reproduce the same temperature ramp for each run; fortunately, this is simple to do using the available TS control software. Data analysis for the TS-PFR is also a more delicate matter; for this purpose, well-tested numerical routines have been integrated into the TS interpretation software to perform the required data filtering and fitting.

It is likely that a combination of signal filtering techniques and appropriate reactor configurations and logging capabilities can be used to optimize the cost-performance specifications of individual TSRs. This will allow custom designed TSRs to meet the needs of researchers in a broad range of laboratories, making this powerful technology widely available and influential in the unravelling of chemical reaction mechanisms.

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